Determination of Acrylamide in Water with Static Injection Chemiluminescence Method

Shouhua Cai[*1], Jing Sun[*2], Xiaoling Yang[*3]

College of Water Conservancy Science and Engineering, Yangzhou University

Yangzhou 225009, China

[*1]caishouhua@aliyun.com; [2]445838380@qq.com; [3]xlyang@yzu.edu.cn

Abstract

In this work, multiple regression analysis was carried out via experiments and data analysis to attain the optimal reacting conditions of the $KMnO_4$-H_2SO_4-Na_2SO_3 chemiluminescence system for acrylamide concentration detection through static injection analysis, i.e. $KMnO_4$:3.8×10^{-4} mol/L; Na_2SO_3:1.8×10^{-3} mol/L; H_2SO_4:3.6×10^{-2} mol/L. In addition, the correlation and the linear regression equation of acrylamide concentration and relative luminous intensity were obtained under the optimal reacting conditions.

Keywords

Multiple Regression Analysis; Static Injection Analysis; Acrylamide; Chemiluminescence

Introduction

Acrylamide (CH_2=$CHCONH_2$) is a small molecule with simple structure. It dissolves well in the polar solvents such as water, methanol and ethyl acetate; but it dissolves poorly in nonpolar solvents including n-hexane and benzene. The maximum solubility can be achieved with water. Numerous experiments have proved that acrylamide is a potential carcinogen and hence it is included in the potential carcinogen list, which is made by IRAC for human beings. According to the studies, acrylamide can influence human body through the digestive tract and the respiratory tract. Drinking water is probably the most predominant exposure route. Both *Drinking Water Standards* (GB5749-2006) and *Surface Water Quality Standards* (GB3838-2002) provide that the residues of the acrylamide must be limited within 0.5μg/L for drinking water. Therefore, it is necessary to establish a method to obtain the amount of acrylamide in water with high sensitivity.

Chemiluminescence is the luminescence phenomenon in some certain chemical reactions. During the process, some certain molecules absorb the energy released by the reaction system and hence are excited to higher energy level. The chemiluminescence occurs as a result of de-excitation when the energy is released as radiation.

Up to now, ECD, FID and HPLC have been widely applied to obtain the amount of acrylamide in water. These methods disadvantage themselves for both low sensitivity and high expense while chemiluminescence is advantageous for a wider linear range with simplicity and high sensitivity. Comparing to the flow injection chemiluminescence method, the static injection chemiluminescence is superior for unlimited luminous time and easily-adjusted operation conditions.

Weak chemiluminescence occurs when $KMnO_4$ and Na_2SO_3 react in acidic solutions. Acrylamide can enhance the luminous intensity effectively for the amino groups and the double bonds can be easily oxidized. Basing on experimental results for chemiluminescence during direct oxidation of acrylamide and its enhancement effect to some benchmark redox systems, Guo et. al. established the flow injection analysis method for acryalamide concentration detection of the $KMnO_4$-H_2SO_4-Na_2SO_3 chemiluminescence system. However, few attempts were made for the static injection method. In preliminary work, the acrylamide was observed to react rapidly with the $KMnO_4$-H_2SO_4-Na_2SO_3 chemiluminescence system and then diffused relatively fast in the flow path. In addition, the enhancive effect of acrylamide was linearly related to its concentration. Based on these features, here we established the static injection chemiluminescence method to detect acrylamide concentration.

Experiments

Instruments and reagents

JJ224BC electronic analytical balance (G&G Measurement Plant); IFFS-A multifunction chemiluminescence detector (Xianruimai Analutical Instruments).

2.5×10^{-2}mol/L KMnO$_4$ solution(0.395g KMnO$_4$ dissolved in 100mL distilled water); 1mol/L H$_2$SO$_4$ solution; 8×10^{-3}mol/L Na$_2$SO$_3$ solution(0.101g Na$_2$SO$_3$ dissolved in 100mL distilled water); 2.5×10^{-2}mol/L acrylamide solution(0.177g acrylamide dissolved in 100mL distilled water); distilled water.

All the reagents listed above were purchased from Sinopharm Chemical Reagent Co.Ltd. with purity of AR. Stepwise dilution applied when needed.

Methods

Firstly, a set of experiments was applied to obtain the optimal concentrations of KMnO4, H2SO4, Na2SO3 in the static injection chemiluminescence system. Multiple regression analysis was adopted for data processing. With the optimal concentration condition, static injection chemiluminescence experiments were then applied with acrylamide solutions of various concentrations to obtain the relationship between acrylamide concentration and relative luminous intensity of the system.

The experimental system was built in a beaker above the PMT of the IFFS-A multifunction chemiluminescence detector. 1mL Na$_2$SO$_3$ solution, 1mL H$_2$SO$_4$ solution and 1mL acrylamide solution were firstly added to the beaker. 1mL KMnO$_4$ was then injected to the system after running the detection software for 5 seconds. The variation of luminous intensity was detected and recorded during the process.

Results and Discussion

Optimization

By exploring the concentrations of 0.010 mol/L~1.00 mol/L for H$_2$SO$_4$, 2.5×10^{-5}mol/L~2.5×10^{-3}mol/L for KMnO$_4$ and 10^{-4}mol/L~10^{-3}mol/L for Na$_2$SO$_3$, the optimal concentration ranges were found to lie in 0.03~0.05mol/L, 2×10^{-4}~4×10^{-4}mol/L and 1×10^{-3}~3×10^{-3}mol/L for H$_2$SO$_4$, KMnO$_4$ and Na$_2$SO$_3$ respectively.

For further optimization, a set of control variable experiments was applied with acrylamide solution of 5×10^{-7}mol/l. The parameters and results are exhibited in TABLE 1; the analysis of variance table linear regression equation is in TABLE 2.

With the significant level of 0.001(p<0.05), a significant ternary quadratic nonlinear regression equation must exist. The expression can be achieved with multiple regression analysis:

TABLE 1 PARAMETERS AND RESULTS

H$_2$SO$_4$mol/L）	KMnO$_4$(mol/L）	Na$_2$SO$_3$(mol/L）	Io	Is	Is-Io
0.03	2×10^{-4}	1×10^{-3}	74	556	482
0.03	2×10^{-4}	2×10^{-3}	28	1519	1491
0.03	2×10^{-4}	3×10^{-3}	36	337	301
0.03	3×10^{-4}	1×10^{-3}	12	946	934
0.03	3×10^{-4}	2×10^{-3}	14	1359	1345
0.03	3×10^{-4}	3×10^{-3}	12	575	563
0.03	4×10^{-4}	1×10^{-3}	12	1011	999
0.03	4×10^{-4}	2×10^{-3}	16	1176	1160
0.03	4×10^{-4}	3×10^{-3}	24	349	325
0.04	2×10^{-4}	1×10^{-3}	24	453	429
0.04	2×10^{-4}	2×10^{-3}	22	1340	1318
0.04	2×10^{-4}	3×10^{-3}	25	552	527
0.04	3×10^{-4}	1×10^{-3}	20	881	861
0.04	3×10^{-4}	2×10^{-3}	57	1555	1498
0.04	3×10^{-4}	3×10^{-3}	12	338	326
0.04	4×10^{-4}	1×10^{-3}	30	672	642
0.04	4×10^{-4}	2×10^{-3}	11	720	709
0.04	4×10^{-4}	3×10^{-3}	11	471	460
0.05	2×10^{-4}	1×10^{-3}	11	480	469
0.05	2×10^{-4}	2×10^{-3}	10	945	935
0.05	2×10^{-4}	3×10^{-3}	11	356	345
0.05	3×10^{-4}	1×10^{-3}	11	598	587
0.05	3×10^{-4}	2×10^{-3}	57	1554	1497
0.05	3×10^{-4}	3×10^{-3}	45	389	344
0.05	4×10^{-4}	1×10^{-3}	75	1553	1478
0.05	4×10^{-4}	2×10^{-3}	12	2157	2145
0.05	4×10^{-4}	3×10^{-3}	11	450	439

TABLE 2 ANALYSIS OF VARIANCE TABLE LINEAR REGRESSION EQUATION

Source of Variation	Sum of Vquares	Degrees of Reedom	Mean Square	F	Significant Level
Regression	9	4841595	537955	8.88	0.001
Goodness of Fit Ttest	18	1401029	77835		
Total Vvariation	27	242625			

$$I = -161 - 10^4 x_1 + 6\times10^5 x_2 - 3.4\times10^4 x_3 -$$
$$1.2\times10^7 x_1 x_2 + 3.8\times10^5 x_1 x_3 - 10^5 x_1^2 - 9\times10^5 \quad (1)$$

Where x_1, x_2 and x_3 are the concentration values (mol/L) of H$_2$SO$_4$, KMnO$_4$ and Na$_2$SO$_3$ respectively. I_o is the luminous intensity of the blank control group; I_s is the biggest luminous intensity of the system.

The optimal concentration conditions can be determined by taking the derivative of formula (1): H$_2$SO$_4$'s concentration is 3.6×10^{-2} mol/L, KMnO$_4$'s concentration is 3.8×10^{-4} mol/L and Na$_2$SO$_3$'s concentration is 1.8×10^{-3} mol/L.

The Standard Curve and the Detection Limit

With the optimal reaction conditions, we tested acrylamide solutions with concentration ranging from 1×10^{-9} mol/L to 2×10^{-5}mol/L. The results showed

obvious linear relationship between the acrylamide concentration and the relative chemiluminescence intensity within the measuring range. In this way, we can get the expression of the relative chemilumine-scence intensity with a specific the acrylamide concentration. The standard curve is shown in FIG 1; the standard curve regression equation and variance are shown in TABLE 3.
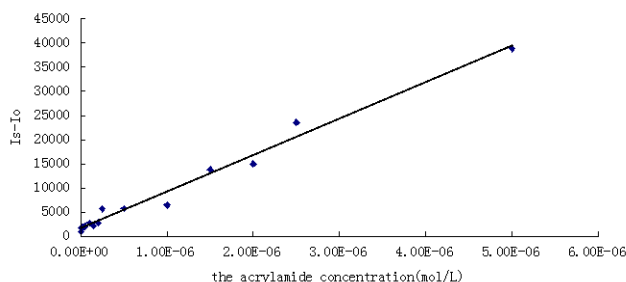

FIG 1 THE STANDARD CURVE

TABLE 3 THE STANDARD CURVE REGRESSION EQUATION AND VARIANCE

The Concentration of Acrylamide (mol/L)	Regression Equation	Variance
$2.5 \times 10^{-9} \sim 5 \times 10^{-6}$	$\Delta I = 7.5 \times 10^{9}\, C + 1673$	0.9838

Note: $\Delta I = I_S - I_O$ is the relative luminescence intensity of the system. C is the concentration of acrylamide solution.

The outcomes of the blank control group are 22, 25, 29, 27, 22, 20, 20, 22, 30, 22, with the standard error of 3.45 for 10 measurements. According to the definition of IUPAC, the detection limit for a method is $3\sigma / N$, where σ is the standard error value for 10 blank measurements, N is the slope of the standard curve. Inserting the σ and N values, the detection limit for our method is 1.38×10^{-9} mol/L.

Interference Tests

Through the large amount of experiment, 1 X ethylenediamine, triethylamine; 10 X Mg^{2+}, Cu^{2+}, Ba^{2+},20 X NH_4^+, Cl^-, Br^-, Cr^{6+}, 50 X Al^{3+}; 100 X CO_3^{2-}, CH_3COO^-, Mn^{2+}, Zn^{2+}, nitroaniline, $H_2PO_4^-$; 500 X Pb^{2+}, Fe^{3+} can influence the result. The effect of metal ions can be shielded by adding EDTA. For organics, the influence can be controlled by distillation or purification with exchange resin.

Conclusion

In this work, the optimal conditions for the static injection $KMnO_4$-H_2SO_4-Na_2SO_3 chemiluminescence system were firstly achieved with multiple regression analysis. Experiments and analysis were then applied with these optimal conditions. Here we established a feasible method to determine the acrylamide concentration via static injection, where alternation of reagents and concentration adjustment were very convenient. The allowable residual concentration of acrylamide in drinking water is 0.5μg/L (approximately 7×10^{-9} mol/L) while the detection limit for our method is much lower, at 1.38×10^{-9} mol/L. Therefore, it can be applied for acrylamide concentration analysis of drinking water.

REFERENCES

al."Determination of acrylamide in foods by GC/MS using 13C-labeled acrylamide as an internal standard."Food Hygienic Society of Japan 43(2002): 371-376

Alain Pitte, Adrienne Périsset, Jean-Marie Oberson."Trace level determination of acrylamide in cereal-based foods by gas chromatography–mass spectrometry." Chromatogr A 1035(2004): 123-130

GB11936-1989, Standard methods for hygienic examination of acrylamide in drinking water sources-Gas chromatography.1989

Guo Gaifen. Flow injection chemiluminescence method for determination of Organic amines Regress Analysis. M.S. diss., Shenyang Ligong University, 2012.

Guschlbauer W. "Nucleic Acid StructureSpringer." New York, Heidelberg, Berlin 35(1976).

I Lyon. ARC. Monographs on the evaluation of carcinogenic risks to humans:some industrial chemicals[M]. Internation-alagency for research on Cancer,1994:389

J S Ahn, L Castle, D B Clarkeet al. "Verification of the findings of acrylamide in heated foods."Food Addit Contam 19(2002): 1116-1124

Lin Jinming. Basic theory and application of the chemiluminescence. Chemical Industry Press.2004

Ono, H., Chuda, Y., Kameyama, M..al. "Anal- ysis of acrylamide by LC-MSWMS and GC-MS in proc- essed Japanese foods."Food Addit Contam 20(2003): 215-220

Shi Zheng , Li Kangmei. "Determination of the Acrylamide

in Water and Wastewater by Capillary Chromatography." China Environmental Monitoring. 14 (1998): 26-28.

Tareke, E., P. Rydberg, P.Karlsson, et al."Analysis of acrylamide, a carcinogen formed in heated foodstuffs." Food Chem 50(2002): 4998–5006

You Haiqin, Li Weibing, Wu Danwen et al. "Determination of trace acrylamide in water by high performance liquid Chromatography."Water purification technology 30 (2011): 72-74

Zhou Kaowen, Xu Zheng."Determination of Trace Formaldehyde in Air With Static Injection Chemiluminescence Method." Beijing Union University 3(2008):68-74

Nemoto S , Takatsuki S ,Sasaki K,

Shouhua Cai was born in China in 1964. He obtained his Ph.D. degree in hydraulic and hydro-power engineering in 2009. His research interests include agricultural soil and water engineering, water ecological engineering and related fields. Currently, he acts as a professor in College of Water Conservancy Science and Engineering, Yangzhou University .